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Title: Aromatic C–H \cdots π , C–H \cdots O and parallel aromatic–aromatic interactions in the crystal structure of meso-tetrakis[4-(benzyloxy)phenyl] porphyrin

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Aromatic C–H \cdots π , C–H \cdots O and parallel aromatic–aromatic interactions in the crystal structure of *meso*-tetrakis[4-(benzyloxy)phenyl]porphyrin

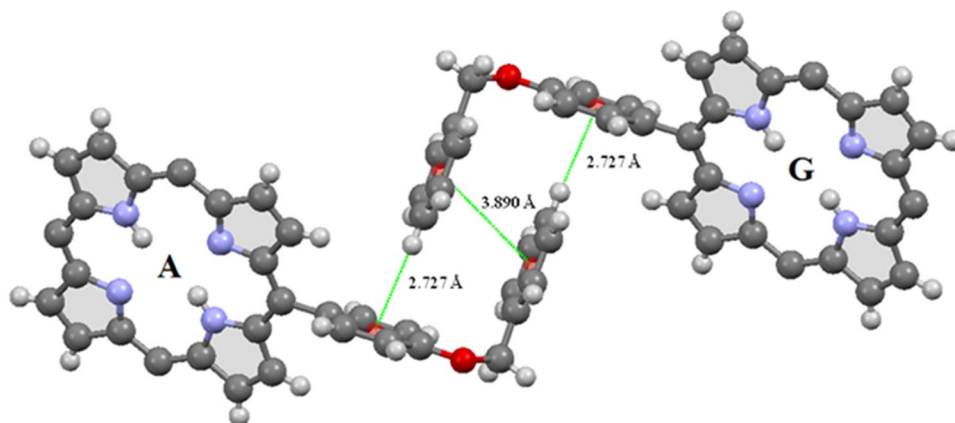
Piotr Kuś¹ · Joachim Kusz² · Maria Książek²

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Abstract

Analysis of the crystal packing of the title porphyrin derivative (C₇₂H₅₄N₄O₄) suggests no classical hydrogen bonds between neighbor molecules. X-ray crystal structure shows that all benzyl units of this porphyrin have close C–H \cdots π weak contacts with phenyl or porphyrinyl units forming a network of porphyrin rings. Also C–H \cdots O and parallel aromatic–aromatic weak interactions play an important role in structure extension. All of these interactions control the crystal packing of molecules. X-ray diffraction was used to perform single crystal analysis. The structure was solved in the triclinic space group P-1, with unit cell parameters: $a = 8.0597(3)$ Å, $b = 11.6862(4)$ Å, $c = 14.2572(5)$ Å, $\alpha = 96.173(3)^\circ$, $\beta = 93.150(4)^\circ$, and $\gamma = 93.679(3)^\circ$, $V = 1329.72(8)$ Å³, $Z = 1$.

Graphical abstract The lack of strong intermolecular hydrogen bonds and presence of numerous weak hydrogen bonds are decisive factors in crystal structure of the examined *meso*-tetrakis[4-(benzyloxy)-phenyl]porphyrin.



Keywords Crystal structure · Porphyrin · Non-covalent interactions · C–H \cdots π interactions · Aromatic–aromatic interactions

Introduction

The color of porphyrins derived from a characteristic central ring results from the electronic properties of these compounds. Particular fragments present in the large central ring cause only negligible deviation from planarity, due to electron coupling in the central moiety, and this was unequivocally confirmed by X-ray analysis. Crystallographic

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structures of many porphyrin derivatives and their complexes have been determined e.g. [1–6]. Such studies may not be possible in case of some porphyrins as they may also occur as amorphous substances. This problem occurs most frequently in case of unsymmetric porphyrins.

Our studies, which have been concerned with synthesis of novel tetraphenylporphyrin derivatives, led to many such compounds. The majority of them did not yield monocystals suitable for crystallographic studies. We also attempted to investigate the structure of amorphous asymmetric porphyrins using synchrotron radiation [7, 8]. Such studies are burdened by severe inconveniences such as access to suitable source of radiation or handling of experimental results.

X-ray study data (CSD) made possible to assess the existence as well as possible value of non-covalent π – π or C–H $\cdots\pi$ interactions between aromatic rings [9–11].

The last few decades noted increased interest in C–H $\cdots\pi$ and π $\cdots\pi$ interactions of *inter*- or *intramolecular* type, especially in crystal structures, as judged from published reports, e.g. [12–20] for C–H $\cdots\pi$ interactions and [10, 21–28] for π $\cdots\pi$ interactions as well as references cited therein. Interactions of this type are especially important for structures described in supramolecular chemistry texts. A very well written overview of such interactions can be found in [29]. Nevertheless, premises underlying their alleged importance in crystallographic structure formation are not entirely clear [30].

These papers include a vast number of references concerning weak hydrogen bonds in crystals formed by various compounds. An essential criterion for occurrence and strength of these bonds are distances between hydrogen atom (in C–H) and the plane of aromatic ring [less than 2.9 Å (sum of van der Waals distances)] as well C–H $\cdots\pi$ access angles (varied from 140°–180°) [13]. Other criteria were adopted for parallel aromatic–aromatic interactions (π – π interactions). Aromatic rings should lie in planes parallel to each other (angle between planes must be less than 10°). Such planes should not be separated by a distance greater than 4 Å, and the distance between centers of aromatic rings should not exceed 6 Å [9].

In the molecule reported herein one could clearly discern such type of interactions and their effect on localization of porphyrin molecules in the crystal structure.

Experimental

^1H NMR spectra were recorded in CDCl_3 using a 400 MHz Varian spectrometer. The peaks were referenced to the residual CHCl_3 resonances in ^1H (7.26 ppm). IR spectra were recorded using Bio-Rad FTS-600 with the samples in the form of KBr pellets. UV–Vis spectra were recorded in chloroform solution using a Genesys 6 (ThermoSpectronic)

spectrophotometer. The single crystal X-ray experiments were performed at 298 K. The data were collected using an Oxford Diffraction kappa diffractometer with a Sapphire3 CCD detector (Oxford Diffraction Ltd., Yarnton, UK). To integrate collected data the CrysAlis PRO software (version 1.171.35.21b, Agilent Technologies) was used. The structure was solved using direct methods with the SHELXS97 software and the solutions were refined using SHELXL97 program [31]. Hydrogen positions were calculated according to geometrical criteria and refined isotropically. All others atoms were refined anisotropically. Crystal data, selected geometric parameters and selected hydrogen-bond parameters are summarized in Tables 1, 2 and 3, respectively.

CCDC 1510250 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.ac.uk/data_request/cif.

meso-Tetrakis[4-(benzyloxy)phenyl]porphyrin ($\text{C}_{72}\text{H}_{54}\text{N}_4\text{O}_4$) was synthesized by condensation of 4-benzyloxybenzaldehyde and pyrrole in propionic acid according to [32, 33]. Violet-colored crystals were obtained using column chromatography of crude product with chloroform and by slow evaporation of concentrated eluent.

MS (ESI): m/z 1039.5 $[\text{M} + \text{H}]^+$, (calcd. for $[\text{M} + \text{H}]^+$ 1039.4).

^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ_{H} , ppm 8.89 (s, 8H), 8.15 (d, 8H), 7.68 (d, 8H), 7.53 (t, 8H), 7.45 (t, 4H), 7.39 (d, 8H), 5.39 (s, 8H), –2.73 (bs, 2H).

UV–vis (CHCl_3): λ_{max} , nm (log ϵ) 421 (4.51), 518 (3.38), 555 (3.25), 593 (3.01), 650 (3.06).

IR (KBr): ν , (cm^{-1}) 3331, 3119, 3033, 2861, 1602, 1503, 1453, 1410, 1390, 1344, 1287, 1218, 1172, 1107, 1081, 964, 928, 912, 878, 856, 834, 805, 786, 735, 695, 642, 618, 590, 556, 530, 501, 455, 422.

Results and discussion

We report here the crystallographic structure of an asymmetric *meso*-tetrakis[4-(benzyloxy)phenyl]porphyrin (Scheme 1). This compound has been known since 1968 [34]. It was prepared using Adler-Longo method (9–10% yield). Twenty years later the same compound was obtained by a method devised and named after Lindsey, with 8–40% yield [35, 36]. We noticed interesting molecular interactions while investigating the structure of this compound. Despite being weak they can affect (or affect) localization of porphyrin rings in the crystal space. In porphyrin molecules there are no functional groups capable of forming strong intermolecular hydrogen bonds. The only suitable moieties are found inside the molecular ring but they are “isolated” by the remaining fragments of the porphyrin ring and its substituents.

Table 1 Experimental details

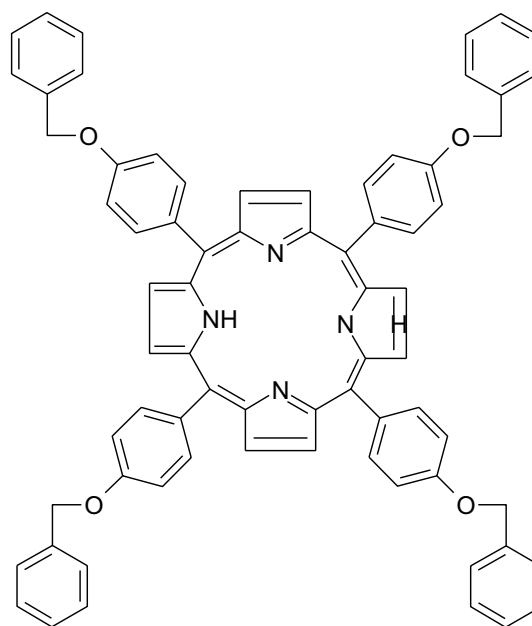
Crystal data	
Chemical formula	C ₇₂ H ₅₄ N ₄ O ₄
<i>M_r</i>	1039.19
Crystal system, space group	Triclinic, <i>P</i> [−] 1
Temperature (K)	298
<i>a</i> (Å)	8.0597 (3)
<i>b</i> (Å)	11.6862 (4)
<i>c</i> (Å)	14.2572 (5)
α (°)	96.173 (3)
β (°)	93.150 (4)
γ (°)	93.679 (3)
<i>V</i> (Å ³)	1329.72 (8)
<i>Z</i>	1
Radiation type	Mo <i>K</i> α
μ (mm ^{−1})	0.08
Crystal size (mm)	0.30 × 0.23 × 0.02
Data collection	
<i>T</i> _{min} , <i>T</i> _{max}	0.997, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	17936 4645 3123
<i>R</i> _{int}	0.052
(sin θ/λ) _{max} (Å ^{−1})	0.596
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.054
<i>wR</i> ²	0.122
<i>S</i>	1.04
No. of reflections	4645
No. of parameters	361
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ^{−3})	0.20, −0.18

Table 2 Selected geometric parameters (Å, °)

C27—O21	1.439 (3)	O21—C27—C28	112.7 (2)
C27—C28	1.503 (3)	O21—C24—C25	125.0 (2)
C44—O22	1.377 (2)	O21—C24—C23	115.7 (2)
C47—O22	1.408 (3)	O22—C44—C43	115.7 (2)
C47—C48	1.508 (3)	O22—C47—C48	109.6 (2)
C24—O21	1.372 (2)	C24—O21—C27	117.75 (19)
		C44—O22—C47	116.20 (19)

Symmetry code(s): (i) $-x+2, -y, -z$

Porphyrin **1** molecule is centrosymmetric with two sets of benzyloxyphenyl units orientation (Fig. 1). Central core of the porphyrin ring is approximately planar with r.m.s deviation of fitted atoms equal to 0.05 Å. The angles between substituent benzene rings and the porphyrin core plane are 61.79(4)° and 65.78(6)°. Besides intramolecular

**Scheme 1** Molecular structure of *meso*-tetrakis[4-(benzyloxy)phenyl]porphyrin**Table 3** Selected hydrogen-bond parameters

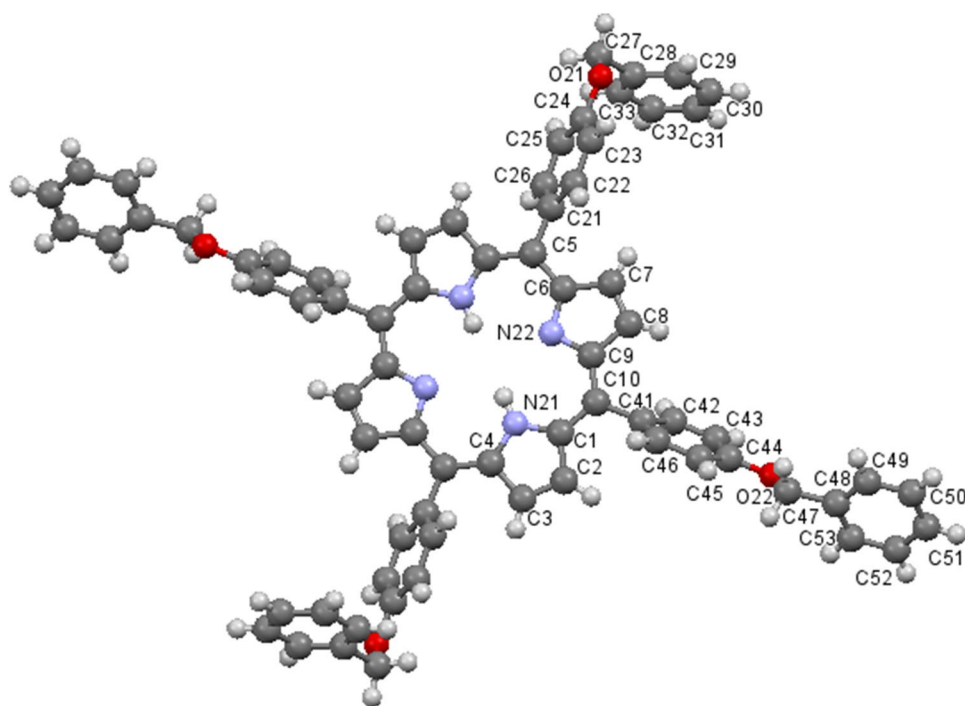
<i>D</i> —H⋯ <i>A</i>	<i>D</i> —H (Å)	H⋯ <i>A</i> (Å)	<i>D</i> ⋯ <i>A</i> (Å)	<i>D</i> —H⋯ <i>A</i> (°)
N21—H21⋯N22 ⁱ	0.86	2.39	2.922 (2)	120.5
N21—H21⋯N22	0.86	2.39	2.924 (2)	120.4

Symmetry code(s): (i) $-x+2, -y, -z$

hydrogen N—H⋯N bonds inside the porphyrin core only intermolecular weak hydrogen bonds are present in this molecule. Detailed information regarding intramolecular hydrogen bonds in the molecules of **1** is given in Table 3.

Packing of *meso*-tetrakis[4-(benzyloxy)phenyl]porphyrin **1** (Fig. 2) is influenced by few weak C—H⋯π, C—H⋯O and face-to-face benzene rings intermolecular contacts forming chains of molecules (in *zig-zag* forms) parallel to (111). The C—H⋯π contacts form the exclusive contribution to the packing, involving two *para*-hydrogen atoms from two benzyloxy groups attached to phenyls in 5 and 15 position of porphyrin ring, respectively (Fig. 3a), and two *meta*-hydrogen atoms from two benzyloxy groups attached to phenyls in 10 and 20 position of the porphyrin ring, respectively (Fig. 3b). Analysis of these C—H⋯π interactions gave C—H⋯centroid phenyl distances of 2.727 Å (H⋯Centroid)/3.628 Å (C⋯Centroid), and C—H⋯centroid porphyrin ring distances of 2.676 Å (H⋯Centroid)/3.523 Å (C⋯Centroid), with corresponding C—H⋯centroid phenyl ring angle of 161° and C—H⋯centroid porphyrin ring angle of 152°, for *para* and *meta* interactions, respectively (Fig. 3a, b). The geometrical categories according to [37] are: both

Fig. 1 The molecular structure of compound **1**, showing atom-labeling scheme. Ellipsoids representing displacement parameters are drawn at the 50% probability level



C–H $\cdots\pi$ interactions is Type I (for C–H $\cdots\pi_{\text{ar}}$ $\alpha = 163.26^\circ$, $\Theta = 83\text{--}91^\circ$; for C–H $\cdots\pi_{\text{pyr}}$ $\alpha = 151.87^\circ$, $\Theta = 92^\circ$).

This (C–H $\cdots\pi$) interaction for rings attached in positions 5 and 15 of the porphyrin **1** causes the two benzene rings of the adjacent molecules' benzyl fragment to be positioned parallel to each other in planes 3.560(1) Å away and centroid–centroid distance of 3.890 Å. Mutual shift of the rings with respect to each other (horizontal displacement of parallel phenyl rings) is ca. 1.38 Å. In [9, 38] the authors calculated the energy of benzene rings' interaction in their various orientations. They concluded that the interaction between two parallel benzene molecules occurs if centroid–centroid distance < 6.0 Å and the distance between the planes of the interacting benzene molecules is < 4.0 Å.

With optimum separation distance of both rings' planes for the above-described parameters the energy of interaction is ca. –2.8 kcal/mol (almost the maximum energy for aromatic–aromatic interactions acc. to [9]).

Similar situation occurs between phenyl rings attached directly to porphyrin rings in positions 10 and 20 (benzyl rings participate in forming C–H $\cdots\pi$ bond of the porphyrin ring). Mutual positioning and shift of phenyl rings are similar in positions both 5 and 15, yet the distance between the ring planes and their centroid–centroid distance are greater (ca. 4.15 Å and ca. 4.4 Å, respectively) (Fig. 3b). These values remain within the range of benzene rings' interaction. The energy of these interactions, although considerably lower, also affects the formation of the molecular system spatial structure.

Another weak contact is C–H \cdots O hydrogen bond between one of the β hydrogen atoms of the porphyrin pyrrole rings and oxygen atoms of the ether bridge between adjacent molecules. The length of these bonds is 2.675(H \cdots O) / 3.485 (C \cdots O) Å, whereas α angle is ca. 146° . This interaction is shown in Fig. 3c.

Torsional angles between porphyrin ring and phenyl rings directly linked to it are: $\pm 59.87^\circ$ and $\pm 65.36^\circ$ for rings in positions 5 and 15 as well as in positions 10 and 20, respectively. Comparing these values leads to the conclusion that deviation of these phenyl rings from the plane of porphyrin ring is affected to a greater degree by hydrogen bonds formed between substituents in positions 5 and 15 than those formed between substituents in positions 10 and 20, respectively. These deviations are not dramatically greater, however, than those occurring in tetraphenylporphyrin (61.0° and 63.1° , respectively) [39].

Distances between planes of porphyrin ring planes are 3.560 Å. Mutual positioning of porphyrin molecules in the crystal is similar to that in porphyrin solutions that do not contain fragments capable of forming strong hydrogen bonds. Weak hydrogen bonds lead to the formation of porphyrin H-aggregates (face-to-face type) in solution, as opposed to J-aggregates (head-to-tail type) formed by porphyrins with strong hydrogen bonds between molecules in solution [40].

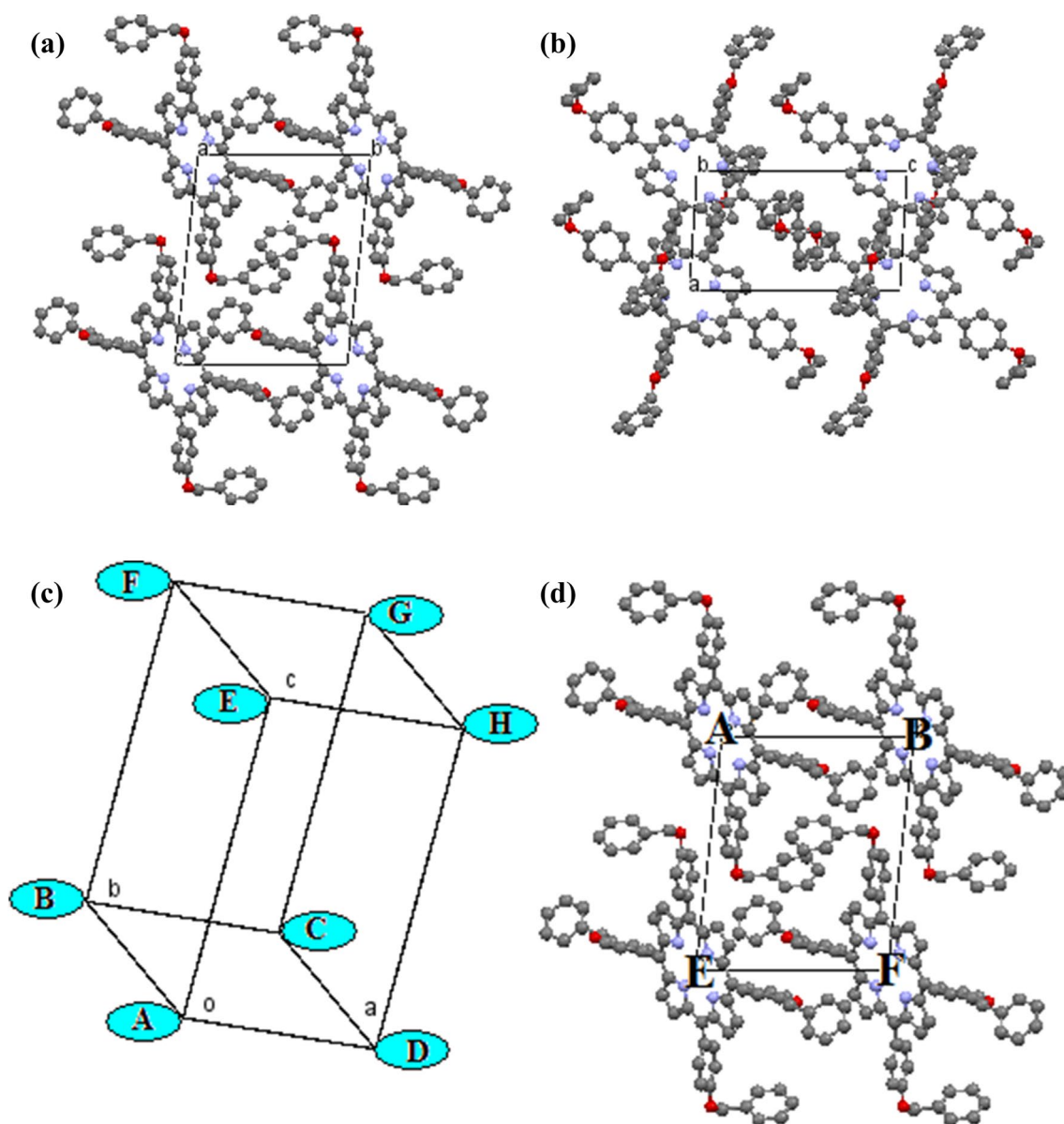


Fig. 2 **a** Packing diagram of compound **1** viewed parallel to the (100) and (010) **(b)** **c** Schematic representation of porphyrin ring disposition in the compound elementary cell. **d** Determination of porphyrin rings along the *a* axis of the elementary cell

Conclusions

Attachment of benzyloxy fragments in *para* position of TPP phenyl rings makes possible additional interactions involving molecules of the starting compound. Such additional interactions accompany formation of crystallographic structures and involve particular porphyrin molecules. The interactions cause the two benzyl rings to move closer (face-to-face), with the distance between parallel planes of both rings going down to 3.6 Å, and with centroid–centroid distance

equal to 3.89 Å. Similar positioning of aromatic rings with respect to each other occurs between phenyl rings directly attached to porphyrin at positions 10 and 20. In this case, however, the distances between the planes of aromatic moieties are greater by ca. 0.5 Å which weakens to a certain degree the π – π interaction of these fragments. Overall, they must contribute to the formation of the crystallographic structure described herein. As exemplified by the fragments of this structure, despite its obvious complexity it is the lack of strong hydrogen bonds and presence of numerous (but weak) hydrogen bonds (the very existence and impact on crystal structure of which continue to be debated) that

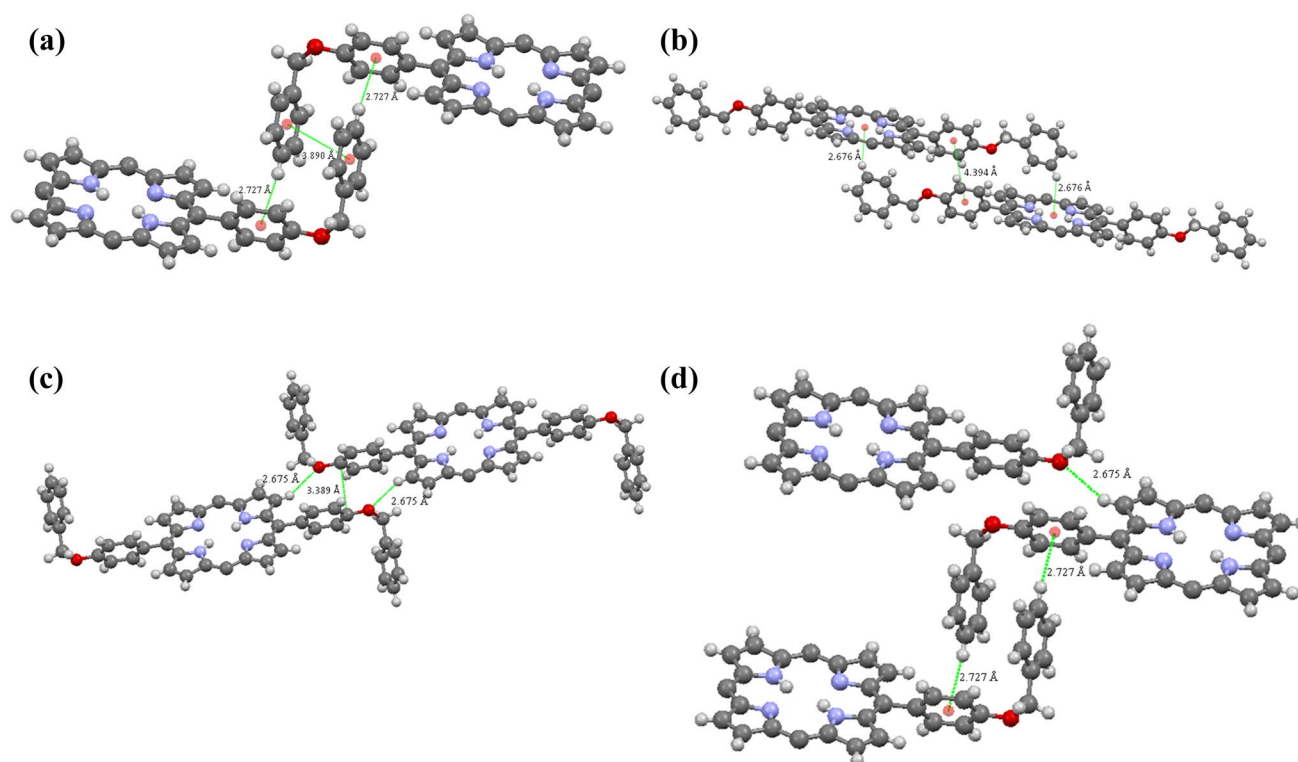


Fig. 3 **a** Illustration of C–H \cdots π hydrogen bonds between two benzyloxyphenyl units of porphyrins located in A and G positions. Substituents in other *meso* positions of porphyrins were omitted for clarity. **b** Hydrogen bond motifs between hydrogen atom of benzene unit and porphyrin core neighbor molecule viewed parallel to the direction of porphyrin rings (in H and F positions; similar situation as in B and D positions). Dashed lines represent hydrogen bonds. **c** Exemplary illustration of C–H \cdots O hydrogen bonds between two benzyloxyphenyl

nyl units located in A and C positions (similar to E and G positions). Substituents in 10- and 20-positions of porphyrins were omitted for clarity. **d** Illustration of both C–H \cdots π weak hydrogen bonds between two benzyloxyphenyl units and C–H \cdots O hydrogen bonds between oxygen atom of benzyloxyphenyl unit and β -hydrogen of porphyrin ring between three molecules of porphyrins located in A, B and G positions. Substituents of 10,15,20-positions of all porphyrins were omitted for clarity

clearly are decisive factors in spatial structure formation of the examined crystal.

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